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Ming Cheng^a; John T. Ho^a; S. W. Hui^b; Ronald Pindak^c; J. W. Goodby^d

^a Department of Physics, State University of New York at Buffalo, Buffalo, New York, U.S.A. ^b

Department of Biophysics, Rosewell Park Cancer Institute, Buffalo, New York, U.S.A. ^c AT&T Bell Laboratories, Murray Hill, New Jersey, U.S.A. ^d School of Chemistry, The University, England

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Electron diffraction studies of surface freezing in hexatic B films

by MING CHENG and JOHN T. HO*

Department of Physics, State University of New York at Buffalo,
Buffalo, New York 14260, U.S.A.

S. W. HUI

Department of Biophysics, Rosewell Park Cancer Institute,
Buffalo, New York 14263, U.S.A.

RONALD PINDAK

AT&T Bell Laboratories, Murray Hill, New Jersey 07974, U.S.A.

and J. W. GOODBY

School of Chemistry, The University, Hull HU6 7RX, England

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Electron diffraction has been used to study the freezing in free-standing hexatic B films of several members of the *n*-alkyl 4'-*n*-alkyloxybiphenyl-4-carboxylate (*nm*OBC) homologous series. It was found that 65OBC exhibits the surface crystal E phase and the accompanying orientational epitaxy previously observed in 75OBC. In 46OBC, the surfaces also appear to attain a higher order ahead of the interior, but retain a six-fold symmetry before the entire film abruptly transforms to the crystal E phase. In 3(10)OBC, the behaviour is similar to that of 46OBC, but the film breaks prior to the observation of any crystal E transition.

1. Introduction

The phenomenon of surface freezing, which is somewhat unique to liquid crystals, was demonstrated previously in the smectic A [1] and nematic [2] phases. Recently, considerable attention has been paid to the study of such a phenomenon involving smectic liquid crystals which exhibit short-range in-plane translational order and long-range bond-orientational order, such as the untilted hexatic B and the tilted smectic I and smectic F phases. These phases are stacked analogues [3-5] of the intermediate hexatic phase predicted to exist by the theory of defect-mediated melting in two dimensions [6, 7]. Surface freezing has been observed in free-standing liquid crystal films near the smectic C to smectic I [8-10] and the smectic A to hexatic B [11, 12] transitions.

In the homologous series of compounds in which hexatic B behaviour has been primarily studied, the *n*-alkyloxybiphenyl-4-carboxylates (*nm*OBC), the hexatic B phase in the bulk is typically found to transform upon cooling to the crystal E phase [13] with the formation of herringbone order. In a series of experiments on free-standing

* Author for correspondence.

films of *n*-heptyl 4'-*n*-pentyloxybiphenyl-4-carboxylate (75OBC) using heat capacity, electron diffraction and X-ray diffraction [14], it was reported for the first time that the hexatic B phase exhibits surface freezing to a state consisting of crystal E surfaces with the interior remaining hexatic B. In order to examine the generality of this surface-freezing phenomenon, we describe here the results of additional electron diffraction studies on the hexatic B to crystal E transition in free-standing films of other members of the *nm*OBC family.

2. Experimental procedure

Electron diffraction was performed in a modified transmission electron microscope with a two-compartment sample chamber [15]. The inner compartment, where the free-standing liquid-crystal film is located, is connected to a nitrogen supply and separated from the main vacuum by an outer compartment. Four collinear apertures in the two compartments allow the incident and diffracted electron beams to pass through. The outer compartment is differentially pumped to remove the small amount of gas leaking from the inner compartment through the apertures, which are sufficiently small to maintain the desired pressure differences among the different compartments. For a typical experiment, the inner chamber is maintained at 30 Torr, the outer chamber at 0.1 Torr, and the microscope vacuum at 10^{-4} Torr. The scattering by the nitrogen gas is minimized to less than 5 per cent by limiting the thickness of the inner chamber to 2 mm. The temperature of the entire thermally insulated, but electrically grounded sample chamber is regulated by a thermoelectric module. Films of *n*-hexyl 4'-*n*-pentyloxybiphenyl-4-carboxylate (65OBC), *n*-butyl 4'-*n*hexyloxybiphenyl-4-carboxylate (46OBC), and *n*-propyl 4'-*n*-decyloxybiphenyl-4-carboxylate (3(10)OBC) were studied. The film thickness was measured using a standard optical reflectance technique [16].

3. Results and conclusions

Our results have revealed that the formation of crystal E surfaces with a hexatic B interior, previously reported only in 75OBC, occurs also in at least one other material, namely, 65OBC. The temperature range in which the surface E phase exists in 65OBC



Figure 1. Electron diffraction pattern from a four-layer film of 65OBC at 62.0°C.

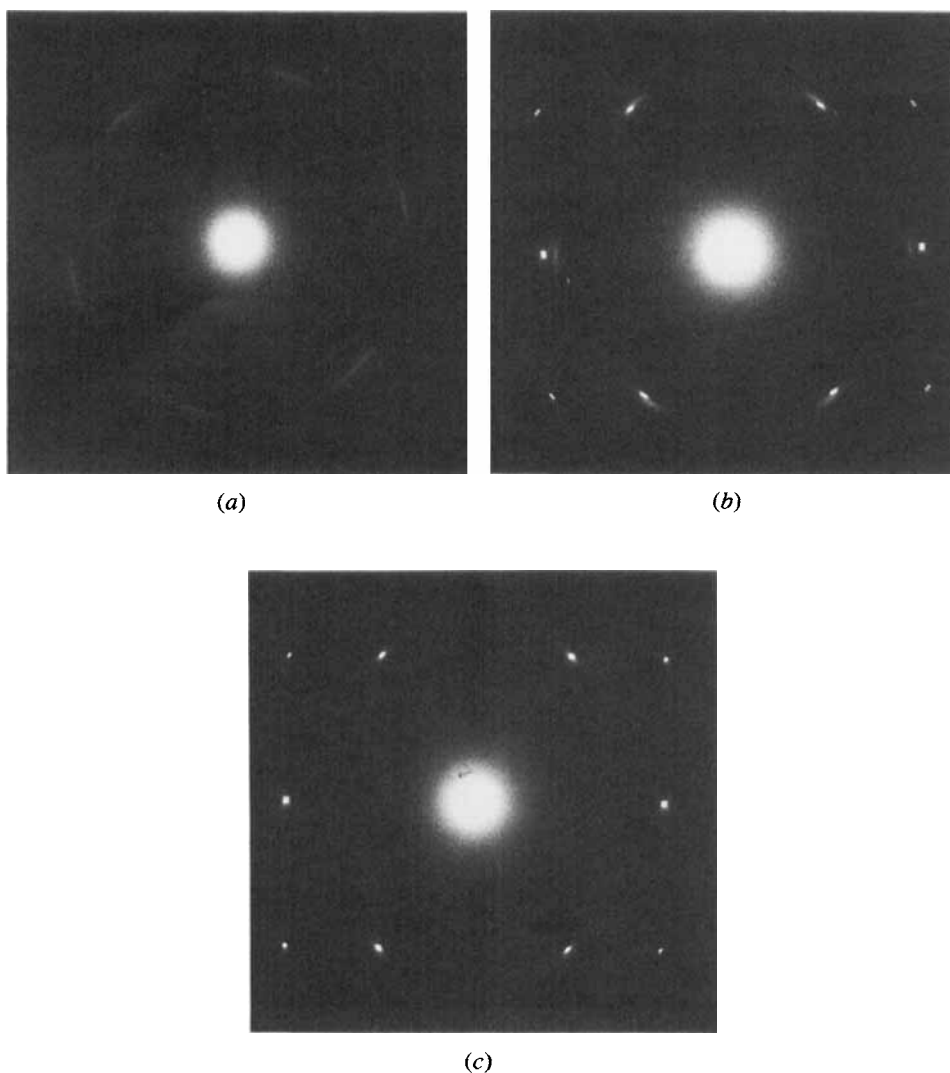


Figure 2. Electron diffraction pattern from a three-layer film of 65OBC at (a) 68.9°C, (b) 65.9°C and (c) 61.7°C.

is somewhat dependent on film thickness, but is generally in the range between 66°C and 61°C, upon cooling from the hexatic B phase. A typical electron diffraction pattern of this phase is shown in figure 1 for a four-layer film of 65OBC at 62.0°C. It reveals the coexistence of the orthorhombic Bragg spots from the crystal E surfaces and the six diffuse arcs from the hexatic B interior. Furthermore, one finds not one, but two sets of orthorhombic Bragg spots which are rotated in opposite directions by a typical angle of 2°–3° with respect to the sixfold bond-orientational axes of the underlying hexatic B interior. Such a rotation is found to be quite prevalent among all the 65OBC and 75OBC samples we have examined, and has been explained by the need to minimize the energy of the strain caused by the existence of the crystal E overlayer on the incommensurate hexatic B substrate [17], analogous to the phenomenon of orientational

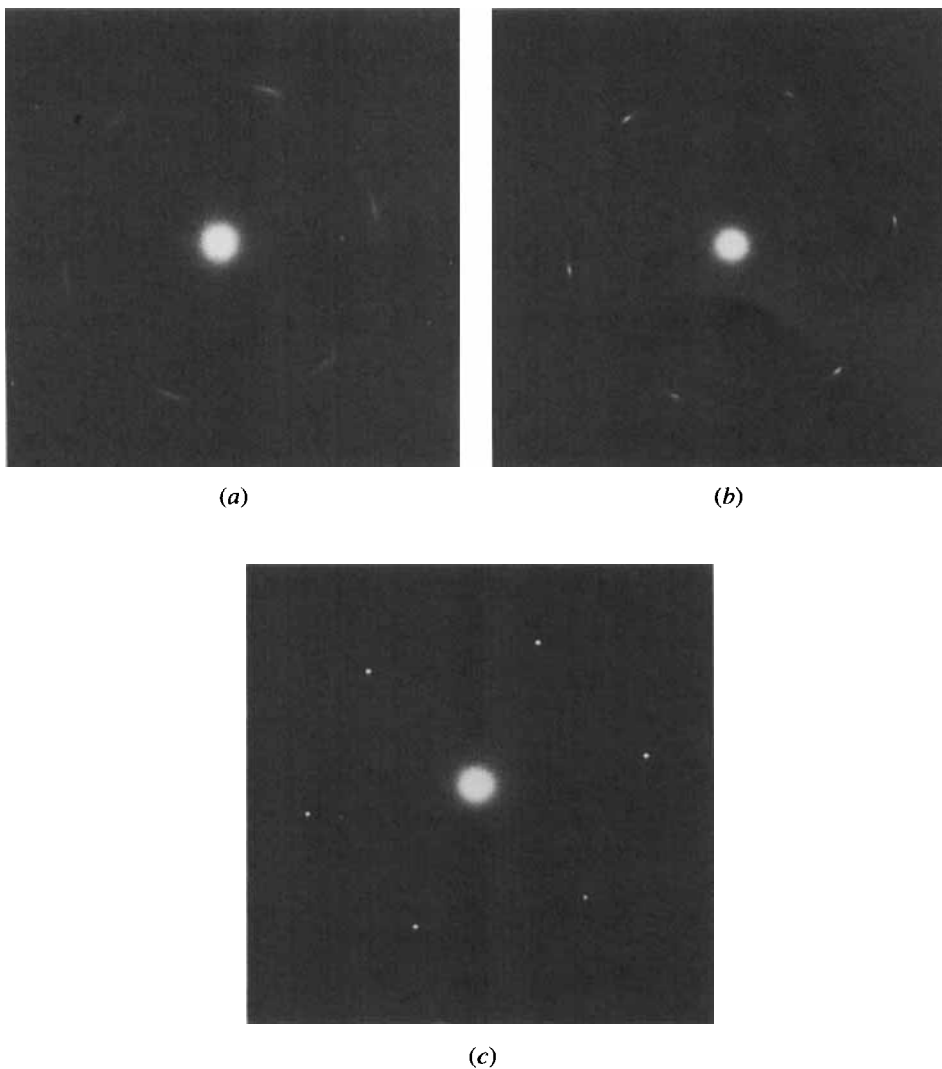


Figure 3. Electron diffraction pattern from a six-layer film of 46OBC at (a) 65.7°C, (b) 56.2°C and (c) 51.9°C.

epitaxy originally predicted for crystalline systems [18, 19] and observed in systems of monolayers of molecules adsorbed on graphite [20–25].

While orientational epitaxy is seen in most 65OBC and 75OBC films in the surface crystal E phase, we have obtained on rare occasions with thinner samples results which exhibit no rotation of the surface crystal E lattice, probably in metastable situations. An example is illustrated in figure 2 for a three-layer film of 65OBC, showing the complete two-step phase transition from the hexatic B to the crystal E. In figure 2 (a) taken at 68.9°C, the entire film is in the hexatic B phase. In figure 2 (b) taken at 65.9°C, the centre layer remains in the hexatic B phase, while the two surface layers have assumed a crystal E lattice, with no rotation with respect to the axes of the underlying hexatic B structure. Finally, in figure 2 (c) taken at 61.7°C, the entire film is in the crystal E phase. Close examination also reveals the existence of unusual diffuse scattering in the neighbour-

hood of the crystal E Bragg spots in figure 2 which might be related to defects in the herringbone ordering [26].

Unlike in 65OBC and 75OBC, we have found no evidence of a surface crystal E phase in 46OBC. The results are illustrated figure 3 for a six-layer film of 46OBC. In figure 3 (a) taken at 65.7°C, the film is in the hexatic B phase, showing the characteristic six diffuse arcs. In figure 3 (b) taken at 56.2°C, the diffraction pattern consists of six diffuse arcs on which are superimposed six sharper spots suggesting the existence of surface layers with stronger order than that of the interior. The surface order is probably still hexatic, but we cannot rule out its being crystalline (hexagonal). We do not yet understand why, as in figure 3 (b), the sharper spots often do not lie precisely along the underlying hexatic axes, since in this instance there is no incommensurability and hence no reason for any orientational epitaxy. Finally, as shown in figure 3 (c), the diffraction pattern abruptly changes at around 51.9°C to one which shows sharp non-hexagonal Bragg spots indicative of a first-order transition of the entire film to the orthorhombic crystal E phase. Thus in the transition from hexatic B to crystal E in 46OBC, the surface layers do appear to develop stronger order ahead of the interior, but they never assume a crystal E state until the entire film does so.

A situation similar to that in 46OBC might be occurring in 3(10)OBC, although in the latter case no transition to the crystal E phase has been observed. Typically, at around 67°C hexatic B 3(10)OBC films develop surface order which is probably still hexatic, but stronger than that of the interior. Both the surface and interior hexatic orders appear to increase as the temperature decreases until the films break at about 54°C, before any transition to the crystal E phase. The behaviour seen using electron diffraction has also been observed using X-ray diffraction [27].

In summary, using electron diffraction, we have examined the lower temperature behaviour of free-standing films of several liquid crystals in which the hexatic B phase exists. We have found that the interesting phenomenon of forming crystal E surfaces prior to complete freezing occurs in 65OBC in addition to the previously reported 75OBC, as well as the accompanying orientational epitaxy. In 46OBC, the surfaces appear to attain a higher order ahead of the interior, while retaining a sixfold symmetry, before the entire film abruptly transforms to the crystal E phase. In 3(10)OBC, the behaviour is similar to that of 46OBC, but the film breaks before any crystal E phase can be observed.

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